Adsorption thermodynamics of aqueous ferric ion onto bio-natural grains of rice

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ABSTRACT

The sorption thermodynamics and equilibrium of inorganic aqueous ferric ion onto Bio-natural Rice Grain (BRG) influence of several factors, such as initial metal ion concentration, the amount of adsorbent and temperatures. Maximum removal finds 99.5 % by using 30 mg L⁻¹ of ferric ions at 37 °C and high dosage concentration (60 g L⁻¹). Langmuir and Freundlich isotherm models can be used to analyze the equilibrium isotherm. The experimental data for the isotherm set are well described by the Langmuir isotherm model ($R^2 = 0.991$). The largest removal of ferric ion, $q_{max}$, is equal 0.7352 mg g⁻¹ at 37 °C. The equilibrium parameter, $R_L$, is greater than 0 but less than 1 indicating that the sorption is more favorable. Thermodynamic studies indicated that the adsorption is a spontaneous ($ΔG = - 3.19058$ kJ mol⁻¹) and endothermic process ($ΔH = + 153.343$ kJ mol⁻¹) with increased entropy ($AS = + 589.163$ J mol⁻¹ K⁻¹), and the rise of temperature can enhance the sorption. The equilibrium data are found fit into the Dubinin-Radushkevich (D-R) model proofing that the calculated values of $E_D$ for the ferric ion is 1.19225 kJ mol⁻¹. This $E_D$ value indicates for a physical adsorption process onto the BRG adsorbent. The new information that can be learned from this study is the use of the rice grains, the natural and safest adsorbent, to remove the ferric ion from the stream of water. The new information in this study suggests that BRG could be used as a natural adsorbent for removing ferric ions from water.

Keywords: Ferric ion, Bio-natural Rice, Grains, Adsorption, Freundlich, Langmuir, Thermodynamic.

1. INTRODUCTION

The industry has become the main source of water pollution of various heavy metals in various compounds. These days, there is a great interest regarding the removal of these metal ions from the aqueous medium. This is because of that the heavy metals dissolved in water have a direct impact on human health, as is in the case in the industry. Although iron is an essential trace element, iron ion considered one of these ions that have an impact on human health in case of its presence in high concentrations. The US Environmental Protection Agency (US EPA) requires that iron ion in drinking water doesn’t exceed 0.3 mg L⁻¹ [1]. Usually, iron concentration in well water does not exceed 10 mg L⁻¹. But, we could find that some countries are still using various iron salts as coagulating agents in water-treatment plants. From another direction, they are also used cast iron, steel, and galvanized iron pipes for water distribution [2]. Through these two ways of both water distribution and/or using the iron salts in the water-treatment plants can raise the concentration of an iron ion in water.

Iron in the water can be associated with a bitter/ metallic taste, Forms rust-colored sediment in water supply water (yellow, red, and orange films of sinks, toilets, tubs, dishes, utensils and even glassware). Furthermore, Iron will cause reddish-brown and discolored clothing during washing. Staining of laundry and plumbing may occur at concentrations above 0.3 mg L⁻¹. Iron can promote the growth of certain kinds of bacteria that resulting in the deposition of a slimy coating on the piping. Furthermore, the high concentration of the iron ion in water can cause anorexia, oliguria, diarrhea, hypothermia, dysphasic shock, and metabolic acidosis [3].

Therefore, it is important to find a method to remove the iron ion from the water safely. At the same time, this method should be economically feasible. Therefore, we find that the scientific talk in this field directed toward the adsorption technique by using natural materials. There are many research works published on this aspect; but, these research works are not important economically with regard to the processing treatment of large amounts of water. The reason returns to the adsorbent materials that are used; wherein they are either high cost or they do not exist in good quantity. Often, these studies clearly focus on the behavior of metal ions in solutions and how they can be linked with the surfaces of the adsorbent. Generally, these studies describe the metal ions trip, starting from the transfer of metal ions from the bulk solution to the end of the trip that related either in bonding metal ions on the surfaces or catching them by the pores of the adsorbent. This information’s can be useful in terms of enhancing and modifying of the adsorbent surfaces as well as increasing efficiency. The most important works, which are belonged using the natural adsorbents for removing iron ions and other heavy metals from water, are granular activated carbon and activated tea waste [4-8], organosilicon compound [9], magnetic zeolite [10], pulp and industrial waste of the papers [11], thioglycolic acid modified oil-palm [12], wild cocoyam biomass [13], coconut husk [14], chitosan coated oil palm shell charcoal [15], lignite [16], chitosan [17], Bengal gram husk powder [18], activated carbon [19-21]. Recently, the significant numbers of natural adsorbents have been used to remove ferric ions from water, whereas these studies achieved good results, such as, zeolite [22], olive cake [23], quartz and bentonite [24], Defatted jojoba [25], feldspar [26] and cotton [27]. One example of adsorbent that could be used in this regard is bio-natural rice grains.
2. EXPERIMENTAL SECTION

2.1. Bio-natural rice grains (BRG). Bio-natural rice grains (BRG) (Egyptian rice grain market type) were ground and then screened into a size fraction of 180 µm by using standard Tyler screen series. Rice grains were washed with excessive amounts of double de-ionized water. The washing process of grains was done by using hot de-ionized water (less than 90 °C) and then the same process are done by using cold water (20 °C), which is repeated three times for each.

2.2. Reagents. All chemicals were used as received as an analytical grade. Fe(NO₃)₃·6H₂O was purchased from Fluka AG (Buchs, Switzerland). HNO₃ (0.1 mol L⁻¹), was purchased from Merck (Darmstadt, Germany). A stock solution of ferric ions was prepared by dissolving an exact amount of Fe(NO₃)₃·6H₂O (±0.01 g) in 990 mL ultra-pure deionized water (18 Ω cm), and then 10 mL of HNO₃ must be added to complete the total volume of solution to 1000 mL. Standard ferric ion solutions of 10, 20, 30, 40, and 50 mg L⁻¹ were prepared by appropriate dilution. An “initial” pH and its subsequent adjustment for all experimental runs were conducted less than 1.20 at the maximum value. The initial pH of the solution was adjusted using 1% HNO₃.

2.3. Apparatus and instruments. The metal concentration in the solution was measured using the atomic absorption spectrophotometer, AAS; (Perkin Elmer Analyst 300). The chemical functional group of the rice grains is detected by FTIR (Thermo Scientific Nicolet IR200 FT-IR). The mixtures were mixed by a thermostatic mechanical shaker at constant temperature (27, 37, 47 and 57 °C (± 1°C), Isothermal Gefellschaft Fur 978). To ensure accuracy in the preparation, analytical balance is used (Sartorius, CP324-S/ management system certified according to ISO 9001).

2.4. Equilibrium studies. The removal of ferric ion was calculated from the mass balance, which was stated as the amount of ferric ion adsorbed onto the BRG. It equals the amount of ferric ion removed from the aqueous solution. Mathematically can be expressed in equations 1-2:

\[ q_e = \frac{(C_i - C_e)}{S} \]  

\[ q_t = \frac{(C_i - C_f)}{S} \]

Where

\[ q_e \]: Ferric iron amount adsorbed on the BRG surface at equilibrium (mg g⁻¹).

\[ q_t \]: Ferric iron amount adsorbed on the BRG surface at a specific time (mg g⁻¹).

Cᵢ: Initial concentration of a ferric ion in the aqueous solution (mg L⁻¹).

Iron occurs in two oxidation states in water, the bivalent or ferrous form, and the trivalent or ferric form. Iron in aqueous solution is subject to hydrolysis. The iron hydroxides formed in these reactions, especially ferric form, have very low solubility. However, the pH affects the iron solution. The most important ionic species of iron that present in water includes Fe³⁺, FeOH²⁻, Fe(OH)⁻², Fe²⁺, and FeOH³⁺, Fe(OH)₃ (aq) present as part of the dissolved iron in natural water at alkaline pH. The Fe(OH)₃ (aq) may exist at pH = 10 and above. Hem and Cropper report the total solubility of iron at pH levels from 4 to 9 [33]. However, in most natural waters, the pH is not low enough to prevent forming the hydroxides. Practically, all the iron ions precipitate as ferric hydroxide under the oxidizing conditions. Another important feature of the chemical behavior of iron in solution is its tendency to form complex ions with inorganic as well as with organic material. These ions are considerably more stable in contrast than the non-complex iron and more may stay in solution soluble.

To the best of my knowledge, it is important to indicate that we did not find any study that can use the bio-natural rice grains for removing the aqueous iron ion, neither Fe²⁺ nor Fe³⁺ ion. In this contribution, we use bio-natural rice grains (BRG) for removing high-level concentration of ferric ion from the aqueous solution. The equilibrium distribution of ferric ion between the sorbent and the solution is important in determining the maximum sorbent capacity. The two isotherm models (Langmuir and Freundlich) will be used to assess the different isotherms and their ability to correlate experimental data. The Langmuir equation is chosen for the estimating the maximum adsorption capacity corresponding to complete monolayer coverage of the BRG surface. The Freundlich model is chosen to estimate the adsorption intensity of the sorbent towards the BRG.

The chemical component of Bio-natural rice grains (BRG) contain starch (90 %), protein (6.2-8.3 %), lipid (1.6 – 2.8 %), moisture (15 – 18 %) and others (Ash, minerals and crude fibers) [28]. It is known that the chemical structure of starch is a complex sugar. Starch is a semi-crystalline polymer, which composes of two polysaccharides: amylose and amylpectin. Amylose, a mostly linear chain that consists of up to 3000 glucose molecules interconnected primarily by α-1,4-glycosidic linkages and is reported to contain a few branched networks. Amylopectin is a large branched polymer with linkages of α-1,4 (as a backbone) and α-1,6 (as bridges that serve as branching points) [29-30]. It is known that the surface structure of bio-natural rice grains has the active –OH entity group of the polymer chain. Considering the exits of–OH entity group gives the starch on the estimated chance of the chemically binding of the metal ion to this group. The bio-natural rice grains contain a cover of rice husk; wherein, Ndazi et al. have reported the chemical and physical properties of rice husk. The rice husk is a cover that encapsulates a grain of rice. This shell makes the cellulose layer. This layer has poor interaction with binding materials [31]. On the other hand, the exit of microsphere through the neutral starch gives the ability to physically adsorb of the metal ions. For example, a novel bio-sorbent rice polish is successfully used for the removal of cadmium (II) from wastewater, where the \( q_{max} \) equal 9.72 mg g⁻¹ [32].

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C_i: Equilibrium concentration or final concentration of a ferric ion in the aqueous solution (mg L^{-1}).

C_f: The final concentration of a ferric ion in the aqueous solution (mg L^{-1}) at a specific time.

S: Dosage (slurry) concentration of the BRG and it is expressed by:

\[
S = \frac{m}{v}
\]

Where v is the initial volume of ferric ion solution used (L) and m is the mass of BRG adsorbent.

The percent adsorption (%) was also calculated using the following equations:

\[
\text{% of Removal} = \frac{C_i - C_e}{C_i} \times 100\% \tag{4}
\]

2.5. Effect of the initial concentration. Adsorption measurements were made by a batch technique at a temperature of 37 \(^\circ\)C. The stopper-plastic flasks containing 50 mL of different initial concentrations (C_i = 10, 20, 30, 40 and 50 mg L^{-1}) of ferric ion and 60 g L^{-1} of BRG were shaken vigorously using a thermostatic mechanical shaker for 3.0 hours. The agitation speed (300 rpm) was kept constant for each run to ensure equal mixing. At the end of the equilibrium time, the flasks were removed from the shaker and then the solution was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

2.6 Effect of the temperature

The adsorption experiments were carried out by shaking vigorously the stopper plastic flasks containing 50 mL of 30 mg L^{-1} of ferric ion solution (initial pH = 1.28) and 60 g L^{-1} of BRG using thermostatic mechanical shaker at constant contact time (3 hours) and agitation speed (300 rpm) with varying temperatures (27, 37, 47 and 57 \(^\circ\)C). At the end of the equilibrium time, the flasks were removed from the shaker and then the solution was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

2.7 Effect of dosage

Adsorption measurements were made by a batch technique at a temperature of 37 (± 1 \(^\circ\)C). Different doses of BRG (2, 8, 16, 20, 40 and 60 g L^{-1}) were placed in a 100 mL stopper plastic flask containing 50 mL of 30 mg L^{-1} of ferric ion solution (initial pH = 1.15). The solutions were shaken vigorously (agitation speed = 300 rpm) using a thermostatic mechanical shaker for 3.0 hours. At the end of the equilibrium, the flasks were removed from the shaker and then the solution was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

3. RESULTS SECTION

3.1. FTIR spectroscopy. The FTIR spectra of bio-natural rice grains show the existence of the carboxylic functional group (1644 cm^{-1}). They show the existence of the hydrogen bonded (−OH) in cellulose fibers (3300 cm^{-1}), which is shifted to the lower frequency by 4 cm^{-1}. The vibration of the C-H bond superimposed to the O-H bond appears at 2928 cm^{-1}. Through careful consideration well in Figure 1 and through the comparison between the pre-adsorption of the curve with the curve after adsorption, we find that there is no significant change in any of the curves.

![Figure 1. FTIR for the Egyptian rice grains before adsorption and after adsorption of ferric ion in the aqueous medium.](image)

Furthermore, we do not see any chemical bond formation. Thus, an adsorption of the ferric ion by the bio-natural rice grains prefers forming of ferric clusters but not individual complexes. From another direction, physical entrapment of ferric ion of the ferric ion as well as minor electrostatic properties of the starch would be characteristic for the adsorption of ferric ion onto bio-natural rice grains. This indicates for weakly coordinating between the active −OH entity functional group of rice grains and the ferric ion. From another direction, this gives similar behavior of physically bounded through microsphere in the neutral starch. This behavior was found matching with previous work of adsorption of copper (II) ion from aqueous solution by starch-grafted polyacrylamide and cross-linked starch grafted polyacrylamide [34].

3.2. Effect of ferric ion concentration. The water resources in Jordan contain varying proportions of iron (Fe^{2+} and Fe^{3+}) ions, starting from the low-level to high. The low level is found in many collected samples starting from 12.2 mg L^{-1} (of the water sample using for industry) to 0.2 mg L^{-1} (of water of tap-water) (see Fig 2). For this reason, we are using 10, 20, 30, 40 and 50 mg L^{-1} to achieve the current and future requirements. Figure 3 shows the removal percentage of the ferric ions using BRG under the influence of these initial concentrations (10, 20, 30, 40 and 50 mgL^{-1}). The maximum removal was ca. 99 % using the initial concentration between 10 to 30 mg L^{-1} at 37 \(^\circ\)C; while it was 40 % (approx.) using high-level of 50 mg L^{-1} at all temperature degrees (27, 37, 47 and 57 \(^\circ\)C). Furthermore, we note from Figure 5 that the temperature significant effect in the case of using low-level concentration (10 mg L^{-1}), while we note the opposite in the case of above 10 mg L^{-1}. The removal efficiency may be that surface saturation related with initial ferric ion concentration. Furthermore, Fe^{3+} ion is adsorbed on the high energy sites at low
concentration. At higher concentration, sites with higher energy are saturated and adsorption starts to the lower energy sites. This is resulting in the decrease in the removal efficiency.

Another reason could be suggested that the presence of high ferric ion quantity, lead to plugging the inlet of BRG microspheres surface; and this prevents ferric ion to enter into the absorbent deeper. This behaviour is connected with the competitive diffusion process of ferric ion onto microspheres of the BRG. The competitive diffusion process could decrease the total microspheres and an increase in diffusion path length. The decrease of micro-spheres in the BRG could contribute to decreasing the adsorbed amount per unit mass [35-37]. This result is compatible with the recent studies, for example, the adsorption of the ferric ion by natural olive cake [23] and cotton [27].

![Figure 2](image-url)  
**Figure 2.** Iron ion concentration-invariant collected samples of tap water.

![Figure 3](image-url)  
**Figure 3.** The effect of initial concentration, namely 10, 20, 30, 40 and 50 mg L⁻¹ of a ferric ion at constant contact time (3 hours), adsorbent dosage 60 g L⁻¹ of ERG (180 µm), Temperature (37 ºC), and agitation speed (300 rpm).

After reaching equilibrium for the adsorption process, we find that the pH value decreases gradually as the concentration of a ferric ion in solution increases as shown in Figure 4. For example, when the concentration of ferric ion was 10 mg L⁻¹ (pHᵢ = 1.13), then the pHᵢ was 1.15 after an adsorption process. While the pHᵢ was 1.11 after an adsorption process using 50 mg L⁻¹ (pHᵢ = 1.36).

### 3.4. Dosage effects

Figure 5 shows the removal percentage of the ferric ion from the aqueous solutions using different doses of BRG (2, 8, 16, 20, 40 and 60 g L⁻¹). This removal experiment was applied at a temperature of 37 ºC. It has been observed from Figure 5 that there is no significant effect of dose rice. Wherein, the largest percentage adsorption of ferric ion is ranging from 98 to 98.5% with a dose of between 2 to 60 mg of BRG at 37 ºC. This unexplained behavior of random results returns to the physical adsorption process, which is difficult to interpret; this is due to several reasons; the most important one is the accumulating of the BRG particulates inside the solution during the adsorption process. This behavior was shown in similar research, for example, the adsorption of the ferric ion by natural olive cake [23] and feldspar [26].

![Figure 4](image-url)  
**Figure 4.** Final (pHᵢ) and initial (pHᵢ) pH values of ferric ion solution of Cᵢ and Cᵢ in constant contact time (3 hours), adsorbent dosage 60 g L⁻¹ of ERG (180 µm), Temperature (37 ºC), and agitation speed (300 rpm).

![Figure 5](image-url)  
**Figure 5.** The effect of ERG adsorbent dosage (2, 8, 16, 20, 40 and 60 g L⁻¹) on the removal ferric ion from the aqueous solution at constant contact time (3 hours), Temperature (37 ºC), agitation speed (300 rpm), Cᵢ = 30 mg L⁻¹.

![Figure 6](image-url)  
**Figure 6.** Final pH values of ferric ion solution as a function of dosage (2, 8, 16, 20, 40 and 60 g L⁻¹) on the removal ferric ion from the aqueous solution at constant contact time (3 hours), Temperature (37 ºC), agitation speed (300 rpm), Cᵢ = 30 mg L⁻¹.

After reaching equilibrium for the adsorption process, we note from Figure 6 that the pH value for each solution is fixed...
after each adsorption process for different doses. This shows that the adsorption process was not affected by the amount of dose BRG. The conductivity decreases significantly for each solution after each adsorption process as shown in Figure 7. This is due to the concentration of the ferric ion that causes the conductivity within the solution. It decreases through the adsorption process by BRG.

![Figure 7](Image)

**Figure 7.** Final conductivity values of ferric ion solution as a function of dosage (2, 8, 16, 20, 40 and 60 g L⁻¹) on the removal ferric ion from the aqueous solution at constant contact time (3 hours), Temperature (37 °C), agitation speed (300 rpm), Cᵢ = 30 mg L⁻¹.

### 3.5. Effect of the temperature

Figure 8 indicates the temperature effect for the removal of aqueous ferric ion using BRG. We have noticed that there has been a slight change in the percentage removal of the ferric ion by increasing the temperature variation in case the use of 20 to 40 mg L⁻¹. However, the maximum percentage removal of ferric ion was at a temperature of 37°C reaching 100 % (approx.). This may indicate to the weak physical interaction of ferric ions with BRG microsphere. But actually, there has been a change in the percentage removal of the ferric ion by increasing the temperature values in the case of using 10 and 50 mg L⁻¹ as shown previously in Figure 3. From another direction, there is a slight change in the sorption equilibrium at high (at 57 °C) and low temperature (at 27 °C).

### 3.6. Thermodynamic studies

The adsorption equilibrium data obtained at various initial ferric ion concentrations are used to assess the adsorption isotherm with the two common isotherm models: Langmuir and Freundlich isotherms. The Langmuir isotherm is based on the theoretical principle that only a single adsorption layer exists on an adsorbent. It represents the equilibrium distribution of ferric ion between the BRG solid and liquid phases. The basic assumption of the Langmuir adsorption process is the formation of a monolayer from the adsorbate (Fe³⁺) on the outer surface of the adsorbent (BRG), afterward, no further adsorption takes place. The Langmuir isotherm for pure component adsorption is described in equation 5 [38]:

\[
\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{1}{q_{max}} C_e
\]

Where, \(q_{max}\) is the maximum removal of the ferric ion per a unit mass of the BRG disorbert (mg g⁻¹), which relates to the adsorption capacity of the BRG. The \(b\) is Langmuir constant (L mg⁻¹), which is exponentially proportional to the heat of adsorption. It relates to the adsorption intensity, which indicates to the interaction forces between BRG surfaces. Therefore, a plot of \(\frac{C_e}{q_e}\) versus \(C_e\), gives a straight line of slope \(\frac{1}{q_{max}}\) and intercept \(\frac{1}{q_{max} b}\) as shown in Fig. 9.

![Figure 8](Image)

**Figure 8.** The effect of temperature (27, 37, 47 and 57 °C) for removing ferric ions from the aqueous solution at a constant initial concentration (30 mg L⁻¹), adsorbent dosage 20 g L⁻¹ of ERG and agitation speed (300 rpm).

The Freundlich adsorption isotherm assumes an exponentially decaying function of site density with respect to heat of adsorption. The Freundlich isotherm is expressed as in equation 6 [39]:

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

The Freundlich isotherm is an indicator of the heterogeneity extent of the adsorbent surface. The Freundlich constants \(K_f\) and \(n\) indicate the adsorption capacity and the adsorption intensity, respectively. Wherein, they are calculated from the intercept and slope of the \(\ln q_e\) vs. \(\ln C_e\) plot.

The Langmuir isotherm constants are calculated and presented in Table 1. The maximum removal of the ferric ion per a unit mass of the BRG (\(q_{max}\)) is 0.7352 mg g⁻¹ at the 37 °C with \(R^2 = 0.9908\). The calculated \(b\) value is equal 4.259 L mg⁻¹, which is consistent with the higher ionization potential of the ferric ion [21]. The \(R^2\) values that were obtained from both Langmuir and Freundlich models at 37 °C were above 0.991 and 0.222, respectively. The experimental data for the isotherm set are well described by Langmuir isotherms. This is due to the increase and higher value of the correlation and regression coefficient from the Langmuir model (\(R^2 = 0.991\)) as shown in Figure 9. The empirical formula of this model was found \(q_e = 1.3602C_e + 0.3193\) with \(R^2 = 0.991\). This indicates for the formation of a mono-layer of the ferric ion around the BRG surface. Furthermore, we have found that the experimental isotherm, as shown in Fig. 10 with \(R^2 = 0.989\), is largely identical to the Langmuir isotherm model. Langmuir model is widely applied to describe the adsorption of several ferric ions onto several adsorbsents like zeolite [22], olive cake [23], cotton [27] and Polyacrylamide grafted activated carbon [40]. It can be observed that the \(d_{max}\) value is very low in contrast to the reported studies as shown in Table 3. This is due to that its adsorption and selectivity adsorption ability is physically or chemically very weak in contrast with others.
where, $T$ is the absolute temperature in Kelvin and $R$ is the gas constant (8.314 J mol$^{-1}$K$^{-1}$). The equilibrium constant ($K_L$) can be calculated by equation 8:

$$K_L = \frac{b \times MA}{n}$$

Wherein, $MA$ is the molar weight of sorbate, and $b$ is the Langmuir constant. The calculated of the equilibrium constant ($k_L$) are shown in Table 1. The value of Gibbs free energy change calculated at 37 °C is found to be $-3.19058$ kJ mol$^{-1}$. The thermodynamic parameters such as enthalpy ($\Delta H$) and entropy ($\Delta S$) were determined by using the following equations [41,42].

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H}{RT}$$

Wherein, $K_L$ is the distribution coefficient of the adsorbate ($\frac{n}{n}$).

“$R$” is a gas constant (= 8.314 J mol$^{-1}$ K$^{-1}$) and $T$ is the temperature (Kelvin). The plot of $\ln K_L$ against $\frac{1}{T}$ (Vant Hoff plot) of the metal ion solution was carried out as indicated in Figure 11, in which the slope ($-\frac{\Delta H}{R}$) and the intercept ($\frac{\Delta S}{R}$) are calculated. The thermodynamic parameters $\Delta H$ and $\Delta S$ are presented in Table 2. Another choice $\Delta G$ can be calculated by using these parameters according to the equation of $\Delta G = \Delta H - T\Delta S$ at the constant temperature.

It is obvious seen in Table 2 that $\Delta G$ are negative values in all cases, revealing that the adsorption processes are spontaneous and thermodynamically favorable. The values of $\Delta G$ become more negative with the increase in temperature, indicating that the adsorption processes would be more favorable at the lower temperature. Generally, the change in free energy for physical adsorption is between $-20$ kJ/mol and $0$, and that for chemical adsorption is between $-80$ and $-400$ kJ/mol [43]. In this study, the values of $\Delta G$ obtained are in the range of 2.0 to 3.0 kJ mol$^{-1}$; suggesting that the adsorption of Fe$^{3+}$ onto EGR solids is physical adsorption.

The positive value of “$\Delta H$” at different temperatures indicates of the endothermic nature of sorption. This is due to that the possibility of the ferrous ion is well solvated. In order for the ferrous ion to be adsorbed, it has to lose a part of its hydration casing. This dehydration process of the ion requires energy. This energy of dehydration supersedes the exothermicity of the ion getting attached to the surface [44]. The increase of the equilibrium adsorption with the increase in temperature means that the adsorption of ferric ion process is controlled by an endothermic process. This phenomenon is characteristic of a chemical reaction or bonding being involved in the adsorption process [45].

The positive value of $\Delta S$ of BRG adsorbent shows the increased of the randomness at the BRG solid-solution interface during the adsorption process. The adsorption reaction could be irreversible. The irreversible adsorption can be inferred by calculating the value of adsorption entropy. Wherein, the positive entropy means: (i) the adsorption process is irreversible; and (ii) sorption favors of forming the stable complex structure. The producing complex bonding and steric hindrance effect, between the ferric ion and active functional group in the BRG, increase the enthalpy and entropy of the system [45].
Wherein, \( b \) is Langmuir constant and \( C_i \) is the initial concentration of the ferric ion. From the data calculated in Figure 12, the \( R_L \) was greater than 0 but less than 1 indicating for the favorable adsorption especially at 37 °C [47]. It is clear shown in Figure 9 that the adsorption matter was slight to be linear. The \( R_L \) values indicate that sorption is more favorable for the lower initial concentration than that of higher concentration. The sorption is more favorable at a lower temperature than that of higher temperature, in order of 37 °C > 47 °C > 57 °C.

**Table 1.** Thermodynamic models of the adsorption isotherm of ferric ion onto ERG.

<table>
<thead>
<tr>
<th>( T, ^\circ C (K) )</th>
<th>( q_{max} ) (mg g(^{-1}))</th>
<th>( b ) (L mg(^{-1}))</th>
<th>( K_f ) (L mol(^{-1}))</th>
<th>( R^2 )</th>
<th>( R_L )</th>
<th>( \frac{1}{n} )</th>
<th>( K_f )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>27 (300)</td>
<td>0.3438</td>
<td>0.1055</td>
<td>5.892</td>
<td>0.2703</td>
<td>0.1-0.000</td>
<td>0.2840</td>
<td>-0.2292</td>
<td>0.2837</td>
</tr>
<tr>
<td>37 (310)</td>
<td>0.7352</td>
<td>4.2590</td>
<td>237.843</td>
<td>0.9908</td>
<td>0.0-0.005</td>
<td>0.5000</td>
<td>-0.1596</td>
<td>0.2234</td>
</tr>
<tr>
<td>47 (320)</td>
<td>0.3573</td>
<td>11.6317</td>
<td>649.572</td>
<td>0.9995</td>
<td>0.0-0.079</td>
<td>0.3589</td>
<td>-0.0226</td>
<td>0.0072</td>
</tr>
<tr>
<td>57 (330)</td>
<td>0.3143</td>
<td>35.7090</td>
<td>1994.169</td>
<td>0.9994</td>
<td>0.0-0.261</td>
<td>0.3496</td>
<td>-0.0368</td>
<td>0.0186</td>
</tr>
</tbody>
</table>

**Table 2.** Thermodynamic parameters of the adsorption isotherm of ferric ion onto ERG.

<table>
<thead>
<tr>
<th>( T, ^\circ C (K) )</th>
<th>(-\Delta G ) (kJ mol(^{-1}))</th>
<th>(-\Delta H ) (kJ mol(^{-1}))</th>
<th>(-\Delta S ) (J mol(^{-1}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>27 (300)</td>
<td>2.16529</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>37 (310)</td>
<td>3.19058</td>
<td>+15334.416</td>
<td>+589.163</td>
</tr>
<tr>
<td>47 (320)</td>
<td>3.56038</td>
<td></td>
<td></td>
</tr>
<tr>
<td>57 (330)</td>
<td>3.97982</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.** List the compression of the parameters of the adsorption isotherm of ferric ion onto the various adsorbent.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>( q_{max} ) (mg g(^{-1}))</th>
<th>( b ) (L mg(^{-1}))</th>
<th>( \Delta G ) (kJ mol(^{-1}))</th>
<th>( R^2 )</th>
<th>( K_f )</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural bentonite (NB)</td>
<td>20.96</td>
<td>0.005</td>
<td>-13.90</td>
<td>0.938</td>
<td>0.202</td>
<td>0.775</td>
<td>0.992</td>
<td>[23]</td>
</tr>
<tr>
<td>Natural quartz (NQ)</td>
<td>14.49</td>
<td>0.004</td>
<td>-13.40</td>
<td>0.961</td>
<td>0.115</td>
<td>0.780</td>
<td>0.996</td>
<td>[23]</td>
</tr>
<tr>
<td>Olive cake (OC)</td>
<td>58.48</td>
<td>0.015</td>
<td>-16.87</td>
<td>0.96</td>
<td>2.164</td>
<td>0.628</td>
<td>0.992</td>
<td>[21]</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

Bio-natural rice grains (BRG) can be used as the low-cost adsorbent for adsorbing of the ferric ion from the water system. The best removal achieved is 99.5 %, in which the low-level concentration, initial concentration of Fe(III) ions (10 mg L⁻¹), dosage (= 60 g L⁻¹ ERG), Temperature (= 37 °C), contact time (= 180 minutes), and agitation speed (= 300 rpm) are applied in the batch sorption system. The adsorption matter was favorable at lower initial concentration and lower temperature used up to 37 °C. The maximum homogeneity adsorption capacities represent the fitting data into the Langmuir model spontaneously with ca. $R^2 = 0.999$. The adsorption of the ferric ion on BRG is spontaneous in nature. Results that have been obtained through the FT-IR and D-R thermodynamic model proved that the adsorption nature of ferric ion on Bio-natural rice grains is weakly chemisorptions process. This approach can be applied and recommended for preparing a natural membrane of rice.

5. REFERENCES

6. ACKNOWLEDGEMENTS

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